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Thermal conductivity and diffusivity of carbon-reinforced polyetherketoneketone composites

Mike Coulson,¹ Eric Dantras ,¹ Philippe Olivier,² Nathalie Gleizes,² Colette Lacabanne¹

¹CIRIMAT, Université de Toulouse, CNRS, UPS, Physique des Polymères, 118 route de Narbonne, 31062 Toulouse cedex 09, France

²Institut Clément Ader, UMR CNRS 5312, Espace Clément Ader, 3 Rue Caroline Aigle, 31400 Toulouse, France

Correspondence to: E. Dantras (E-mail: eric.dantras@univ-tlse3.fr)

ABSTRACT: Heat transfer properties play an important role in processing of polyetherketoneketone (PEKK)/carbon fiber (CF) composites. Accordingly, thermal conductivity and diffusivity of PEKK, PEKK/glassy carbon (GC), and PEKK/CF composites have been studied. Observed increase in conductivity and diffusivity with carbon filler addition was analyzed using the Maxwell–Eucken model. PEKK/GC composites with low carbon fraction indicated good fitting experimental points of the model, indicating good dispersion of particles. For PEKK/CF composites, the thermal conductivity and diffusivity increase is a reflection of a decrease in porosity. Results as observed from the model points to a homogenous dispersion within the PEKK/CF composites as well.

KEYWORDS: CFRP; diffusivity; PEKK; thermal conductivity

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INTRODUCTION

The use of carbon in polymer composite is recurrent for the improvement of specific properties.^{1–4} Carbon fibers (CFs) are often used as mechanical reinforcement for polymer composite.^{5–8} Polyetherketoneketone (PEKK)/CF composites could be attractive structural materials if the automation of the processing is possible. The most promising technology for realizing future parts for aero-nautics and space is the automated fiber placement technology with laser heating. A tape of carbon fiber impregnated with PEKK powder was developed to be deposited by a fiber placement robot. During this deposit, it will be important to understand heat transport phenomena in such complex materials. Thermal conductivity and thermal diffusivity are widely studied in the field of polymers and their composites.^{9–15} Several works were devoted to the temperature dependence of thermal conductivity and thermal diffusivity of polymer composites.^{16–19} In polymer composites, a decrease in the thermal diffusivity and an increase in thermal conductivity with the increase in temperature were observed.^{10,20–24} The introduction of fillers modifies the thermal properties of polymers. The composite shows thermal conductivity and thermal diffusivity higher than for the polymer.^{15,25}

Scant information is available on polyaryletherketone (PAEK) studies; however, Choy *et al.* on PEEK/short-fiber composites obtained a thermal conductivity of $0.02 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for PEEK at $25 \text{ }^\circ\text{C}$ and increase in conductivity as a function of temperature was

observed.^{21,26} In addition, PEEKs have been reported to show a decrease in thermal diffusivity with increasing temperature^{20,21} (at $25 \text{ }^\circ\text{C}$, polymers thermal diffusivity is between 0.05 and $0.3 \text{ mm}^2 \text{ s}^{-1}$ ^{27–31}). Within available literature, it appears as if these parameters may have not been studied in the case of PEKK.

The use of a fixed PEKK volume fraction for manufacturing carbon fiber-reinforced polymers (CFRPs) makes it difficult to understand the contribution of carbon on thermal parameters, that is why a comparative study with PEKK and vitreous carbon has been carried out. The glassy carbon is a highly pure carbon black with spherical morphology (aspect ratio close to 1). The intrinsic thermal conductivity of glassy carbon particles³² can be as high as $35 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$. An increase in thermal conductivity was noted with the addition of carbon fillers, thermal conductivities of about $0.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ were measured^{32,33} for load ratios between 30% and 40% in volume. Several CFRP studies have shown that the increase in conductivity and thermal diffusivity is a function of the carbon fiber concentration.^{21,23,24} Fujishiro *et al.*²⁴ showed that the thermal diffusivity is higher in the direction parallel to the fibers than in the transverse direction. Diffusivity values of $0.45\text{--}0.55 \text{ mm}^2\cdot\text{s}^{-1}$ at $50 \text{ }^\circ\text{C}$ for epoxy composites/continuous carbon fibers have been reported.^{34–36} Choy *et al.*²¹ studied the diffusivity of PEEK/short-carbon fiber composites and obtained values between 0.7 and $1 \text{ mm}^2 \text{ s}^{-1}$ at $50 \text{ }^\circ\text{C}$; this greater diffusivity has been attributed to the random orientation of the short fibers.

EXPERIMENTAL

Materials

Polyetherketoneketone. PEKK KEPSTAN (Figure 1) was supplied by ARKEMA France in powder (20 μm).

Physical properties of PEKK are defined by terephthalic/isophthalic precursor ratio (T/I ratio). PEKK KEPSTAN presents a 70/30 T/I ratio.

Carbon Fillers. Glassy carbon. The vitreous carbon from Sigma-Aldrich (Saint Louis, Missouri, USA) is 99.95% pure with spherical particles averaging 12 μm in diameter. It was made by the pyrolysis of furfuryl alcohol.³⁷ We thus had model samples with controlled aspect ratio fillers and variable volume fractions.

Carbon Fiber. Unidirectional carbon fibers Toray's Torayca T700 were used. Fibers were used unsized. T700 fibers with a carbon content of 93%,³⁸ possess high mechanical properties, showing a tensile modulus of 135 GPa.

Composite Preparation. PEKK/glassy carbon composites. PEKK and GC were dispersed in ethanol by sonication for obtaining dispersion. After evaporation of the solvent, the powder was molded at 370 °C. Composites with volume fractions comprised between 5% and 45% in volume were prepared.

PEKK/CF composites. After impregnation, composites with a 40 vol % of PEKK were obtained. A "reference" PEKK/CF composite was realized by draping and consolidation in autoclave. Other PEKK/CF composites were prepared by automated placement fibers. After the laser deposit, a PEKK/CF composite was obtained with a mechanical strength. Porosity could remain inside composites, which imply an additional consolidation step after deposit (autoclave/hot press).

Methods

Guarded Hot Plates Method: Thermal Conductivity. The thermal conductivity was measured using the guarded hot plates method. The main advantage of this technique is that the thermal conductivity is deduced from the Fourier equation: an accuracy of 5% is obtained. The measure does not involve density that cannot be determined with a good accuracy in heterogeneous materials like composites. A stationary unidirectional heat flow was created within the sample. All the assembly was equilibrated by the guard at the temperature of the measurement. The thermal resistance of the sample was determined using the relation 1:

$$R_{\text{Sample}} = F \frac{T_u - T_m}{T_u - T_l} - R_{\text{cal}} \quad (1)$$

where R_{sample} is the thermal resistance of the sample, R_{cal} is the thermal resistance of the calorimeter, and F is the calibration factor of the device. The three temperatures correspond, respectively, to T_u (upper plate temperature), T_l (the lower plate temperature), and T_m (temperature of the material). The thermal conductivity λ is then determined from eq. (2):

$$\lambda = \frac{e}{R_{\text{sample}}} \quad (2)$$

where e is the sample thickness. The device used is the DTC 300 thermal conductivity meter from thermal analysis instrument. The disk-shaped samples have a diameter of 50 mm and a thickness of 2 mm. In order to optimize the heat transfer through the sample, it is covered with a thermal paste (silicone/alumina), which improves the contact with the plates. The measurements were performed during heating by temperature step. A change of standard must be carried out at 100° C, so it is not possible to carry out continuous measurements from ambient to high temperatures. The measurements were performed under air at 25 °C, and then from 140 °C to 230 °C by steps of 10°. The high temperature range was chosen in order to be as close as possible to the conditions of implementation of the CFRP. However, the limits of the equipment and the used thermal paste imposed a maximum temperature of 230 °C.

Laser Flash Method: Thermal Diffusivity. The Laser Flash method is the only one that allows us to reach thermal diffusivity. The Laser Flash Analyzer LFA 447 from Netzsch³⁹ was used. A hotplate disposed in the sample holder encouraged measurement at the desired temperature. A laser pulse is then sent to the lower face of the sample and the infrared detector located on the upper face transmitted the temperature signal of the sample as a function of time. The samples were squares of 10 mm \times 2–4 mm thick. The thermal diffusivity measurements were performed on PEKK/glassy carbon and PEKK/CF composites at a temperature of 50 °C with 20 °C increments up to 270 °C. The measurements were performed under air.

RESULTS AND DISCUSSION

Thermal Conductivity of PEKK/Glassy Carbon Composites

Influence of Glassy Carbon Volume Fraction. Carbon glassy particles, with an aspect ratio (ξ) close to 1, are shown in Figure 2.

The evolution of the thermal conductivity λ of PEKK/GC composites is measured at 25 °C as a function of carbon volume

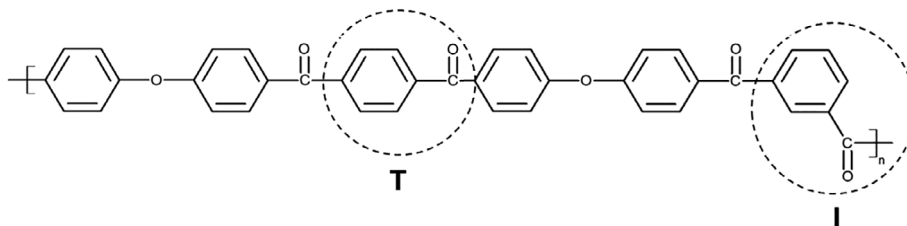


Figure 1. Molecular structure of PEKK with para and meta links.

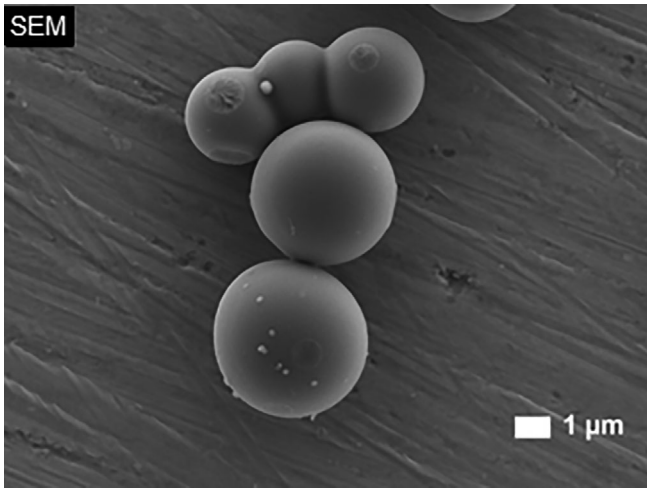


Figure 2. SEM image of GC.

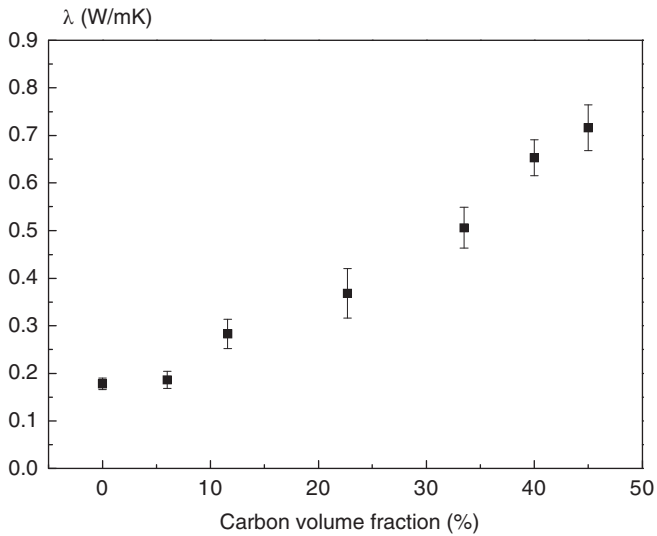


Figure 3. Thermal conductivity of PEKK/GC composite as a function of carbon volume fraction.

fraction (Figure 3). Carbon volume fractions were chosen between 0 vol % and 45 vol % to study the thermal behavior from low-volume fraction to volume fraction as close as possible to CFs volume fraction of PEKK/CF composite. For PEKK/GC composite, 45 vol % glassy carbon is the limit. Above this value, the composite is brittle and cannot be processed for measurements. The measurements are performed three times for each sample; the values reported in Figure 3 are the average of the three measurements.

The thermal conductivity of PEKK is $0.178 \text{ W.m}^{-1}.\text{K}^{-1}$. This value is consistent with those reported in the literature for

Table I. Thermal Conductivity of PEKK/CF Composite at 25°C

	PEKK/CF Reference	PEKK/CF ₀ consolidation	PEKK/CF Autoclave	PEKK/CF Pressed
$\lambda \text{ (W.m}^{-1}.\text{K}^{-1})$	0.654	0.283	0.490	0.538

different polymers: around $0.2 \text{ W.m}^{-1}.\text{K}^{-1}$ at room temperature.^{21,39} It should be noted that it is close to PEEK value²⁰ ($0.24 \text{ W.m}^{-1}.\text{K}^{-1}$).

The introduction of vitreous carbon into the PEKK matrix results in an increase of thermal conductivity. This complex behavior will be described by analog models. This analysis will be presented later in the section on isotherm analog models. For the PEKK/GC composites with the highest content (45 vol % of carbon), a value of $0.716 \text{ W.m}^{-1}.\text{K}^{-1}$ is reached. The increase in thermal conductivity with the introduction of glassy carbon is low compared to the values reported in the literature, for a compacted powder of glassy carbon²²: between 4 and $6 \text{ W.m}^{-1}.\text{K}^{-1}$.

Thermomechanical History Effect of PEKK/CFs Composites.

The PEKK/CF samples were studied by the guarded hot plate method at 25°C . The conductivity values for these samples are reported in Table I.

A PEKK/CF composite realized by a draping and consolidation in autoclave was used as reference to evaluate the quality of the composites produced by laser deposit. For this “reference PEKK/CF” composite, a value of $0.654 \text{ W.m}^{-1}.\text{K}^{-1}$ is indicated. This value is considered as the optimum conductivity value obtainable, according to our data, with this type of PEKK/CF composite. In Table I, measurements were made on a non-consolidated sample (after laser deposit) and on a consolidated sample by hot press. Composites produced by laser deposit have a lower thermal conductivity than the reference composite, which implies a better consolidation of the reference composite. In addition, the thermal conductivity of the composites increases with the level of consolidation with a conductivity of $0.283 \text{ W.m}^{-1}.\text{K}^{-1}$ for the nonconsolidated composite and a value of $0.538 \text{ W.m}^{-1}.\text{K}^{-1}$ for the hot-press consolidated composite. This result implies that the internal connectivity of the material plays a major role in heat transfer.

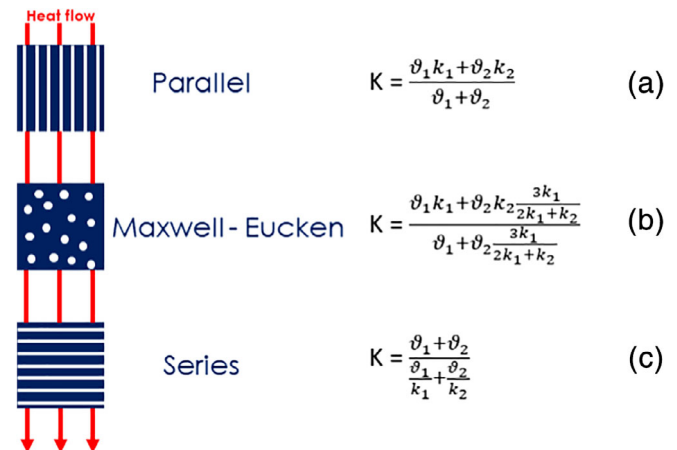


Figure 4. Analog models associated with the evolution of the thermal conductivity as a function of the carbon volume fraction. Conductivity equations correspond to model: (a) parallel, (b) Maxwell–Eucken and (c) series.^{9,40} [Color figure can be viewed at wileyonlinelibrary.com]

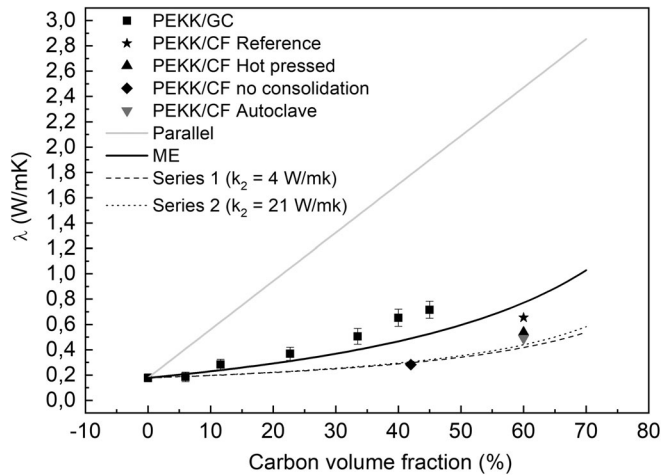


Figure 5. Thermal conductivity λ , as a function of carbon volume fraction. The gray and black continuous lines correspond to the parallel and Maxwell–Eucken models respectively; the dashed and the dotted lines corresponds to the series 1 and series 2 models, respectively.

Isothermal Analog Model. To better understand the thermal behavior of the PEKK/GC and PEKK/CF composites, the experimental points were compared to analog models.⁴⁰ The three models used, as well as the equation associated with λ (or K) for each model are shown in Figure 4.

Analog models take into account the orientation of the heat flux, the volume percentage of the two components (ν_1 and ν_2) and the thermal conductivity of the components (k_1 and k_2).⁴⁰ The values k_2 and ν_2 being associated with the most thermally conductive constituent, here the carbon filler (GC or CF). For all three models, the value of k_1 is $0.178 \text{ W.m}^{-1}.\text{K}^{-1}$ (measured value for PEKK) and the value of k_2 is $4 \text{ W.m}^{-1}.\text{K}^{-1}$ for GC and $21 \text{ W.m}^{-1}.\text{K}^{-1}$ for CFs.⁴¹

The parallel model corresponds to a succession of polymer layers and carbon stacked on each other; the measurement is carried out in the plane of the layers. The series model is also a succession of polymer and carbon layers, but the measurement is performed in the direction perpendicular to the layers. The Maxwell–Eucken model corresponds to spherical particles ($\xi = 1$) dispersion in a matrix. This last model does not take into account interactions between particles so that it is more suited to low loading with well-dispersed fillers. The different analog models predictions, as well as the experimental points of the PEKK/GC and PEKK/CF composites, are plotted in Figure 5.

The parallel model is well above the experimental points, which is consistent with measurement along the longitudinal direction of the oriented layers. This case can be associated with polymer/CF composites by taking the measurement in the longitudinal direction of the fiber. In this study, this type of measurement is not feasible with these composites (quasi-iso multiplies); the device imposes the sampling geometry. The series model is below the experimental points corresponding to the PEKK/GC composites. The conductivity values of PEKK/pressed CF composites are close to the series model, which is consistent with transversal measurement of successive layers: PEKK and continuous carbon fibers.

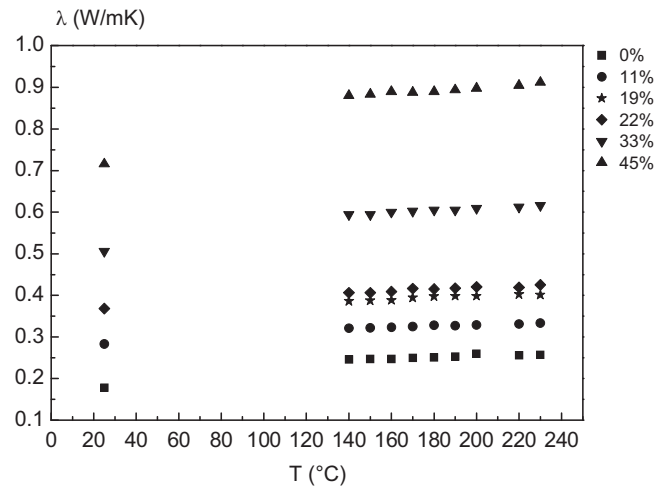


Figure 6. Thermal conductivity λ of PEKK/GC composites as a function of temperature. The cartoon indicates the carbon volume fraction.

Two series models were used: the first with $k_2 = 4 \text{ W.m}^{-1}.\text{K}^{-1}$ to compare the values with the composites PEKK/GC and the second $k_2 = 21 \text{ W.m}^{-1}.\text{K}^{-1}$ for PEKK/CF composite. The difference between the two models is weak, which implies that the thermal conductivity values depend mainly on the thermally insulating phase.

The filler volume fraction of the nonconsolidated PEKK/CF composite was evaluated at 44 vol %, taking into account the porosity determined by hydrostatic weighing at $27.3\% \pm 1\%$. Porosity values were also checked by X-ray tomography. By studying the gray levels, the porosity ratio has been determined. An overall porosity of $25.7\% \pm 3\%$ is obtained for nonconsolidated PEKK/CF composite. This porosity rate is consistent with the result obtained by hydrostatic weighing measurement.

Non-consolidated PEKK/CF composite processed by laser deposit shows a behavior close to the series model, with a thermal conductivity of $0.283 \text{ W.m}^{-1}.\text{K}^{-1}$. The PEKK/CF sample prepared by laser deposit and hot pressed has a thermal conductivity of $0.538 \text{ W.m}^{-1}.\text{K}^{-1}$ while remaining close to the series model.

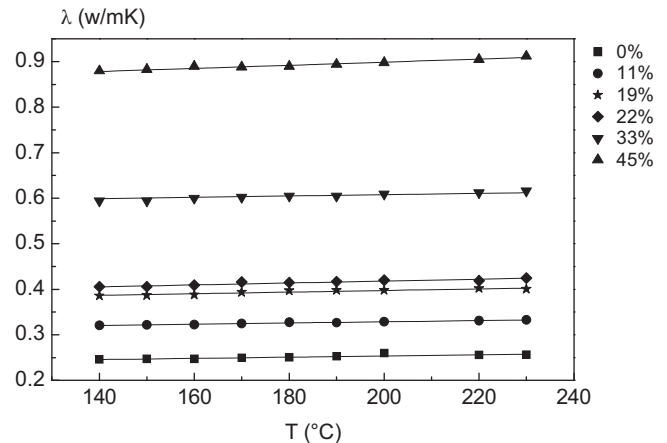


Figure 7. Thermal conductivity λ of PEKK/GC composites as a function of temperature. The solid lines correspond to the fitting.

Table II. Equations Parameters Describing the Behavior of λ as a Function of T

$\lambda = a.T + b$	$a (\times 10^{-4})$	b
PEKK	1.68	0.227
PEKK/11% GC	1.70	0.302
PEKK/19% GC	1.74	0.362
PEKK/22% GC	2.08	0.376
PEKK/33% GC	2.29	0.563
PEKK / 45% GC	3.41	0.831

The thermal conductivity is higher for the reference composite with fiber, $\lambda_{\text{Ref}} = 0.654 \text{ W.m}^{-1}.\text{K}^{-1}$, which corresponds to a behavior closer to the Maxwell–Eucken model. For this composite, the porosity is determined by hydrostatic weighing at <1 vol %. But the higher value of conductivity cannot be explained only by a better consolidation which slightly increases the conductivity. In this case, the increase in thermal conductivity has been associated with a better distribution of the matrix between the fibers, which corresponds, in a 2D transverse model, to a disk dispersion in a matrix. Thus, there is an analogy with a dispersion of spherical particles, which explains the proximity of the experimental points to the Maxwell–Eucken model. In the case of composites developed by laser deposit, the lower thermal conductivity could be explained by a poor distribution of the matrix in the fibers which would give rise to differentiated layers of fibers and polymer (as in the case of the series model). Experimental points of the PEKK/GC are well described by the Maxwell–Eucken model, for low carbon volume fraction, which implies a good dispersion of the particles in the PEKK matrix. The higher thermal conductivity values for higher carbon content (> 20%) can be explained by the existence, among carbon particles, of contacts not taken into account by the model.

Evolution with Temperature

Fillers Volume Fraction Effect. The effect of the carbon particles introduction on the thermal conductivity behavior with temperature was studied on PEKK/GC composites. The measurements were performed on composites loaded between 0 vol % and 45 vol %, for temperatures between 25 and 250 °C. Measurements are reproduced three times and the values shown in Figure 6 are the average of these three points.

Thermal conductivity increases slightly with temperature for all PEKK/GC composites. This type of behavior has already been observed by Choy *et al.* on PEEK and PEEK/CF composites.^{21,39} On polymer matrix and carbon particle composites, Lin *et al.* and Hung *et al.* observed linear behaviors of thermal conductivity with temperature.^{42,43} We studied the evolution of thermal conductivity as a function of the particle ratio with empirical model. An affine relationship was used to describe our experimental points between 140 and 230 °C (Figure 7).

Equations parameters describing the variation of thermal conductivity versus temperature are reported in Table II.

The evolution of the thermal conductivity versus temperature is directly related to the carbon volume fraction. Although there is

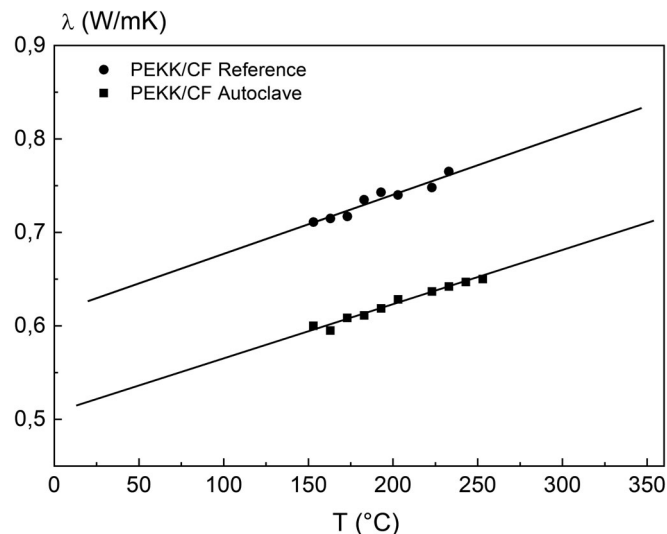


Figure 8. Thermal conductivity λ of PEKK/CF reference composites and PEKK/CF produced by laser deposit, as a function of temperature.

a slight increase, the slope looks to be constant for the first three volume fraction and increases rapidly with increasing loading. Therefore, the slope increase could be related to contacts between spherical particles that favors heat transfer.

Thermodynamic History Effect. The temperature behavior was studied on PEKK/CF composites. The measurements made on the PEKK/CF reference composite and the PEKK/CF autoclave consolidated composite are shown in Figure 8. A porosity of 4% for both samples was determined by hydrostatic weighing.

A monotonous increase is observed on the PEKK/CF composites in the studied temperature range. The difference in thermal conductivity between the two composites is due to the porosity of the PEKK/CF composite consolidated in autoclave and a better

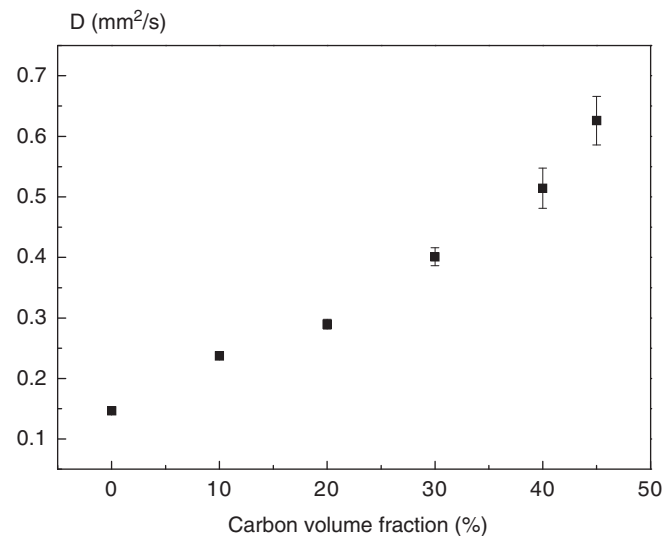


Figure 9. Thermal diffusivity D of PEKK/GC composite as a function of carbon volume fraction.

Table III. Thermal Diffusivity D of PEKK/CFs Composites at 50 °C

	PEKK/CF Reference	PEKK/CF Autoclave	PEKK/CF Pressed
D (mm ² .s ⁻¹)	0.603	0.495	0.517

distribution of the polymer within the fibers in the reference composite.

Experimental points of the PEKK/CF composite consolidated in autoclave are described by a straight line with a slope of 5.80×10^{-4} . The straight line describing points corresponding to the reference PEKK/CF has a slope of 6.39×10^{-4} . It can be seen that for the same volume content of fibers, the slope increases slightly with the connectivity variation.

Although the thermal conductivity values obtained for the PEKK/CF composites are lower than those obtained for the most loaded PEKK/GC composites, the resulting slopes are higher. This confirms that the evolution of the conductivity is related to the amount of carbon in the composite, with a slope that increases with carbon volume fraction.

Thermal Diffusivity

Filler Volume Fraction Effect. The evolution of thermal diffusivity as a function of the carbon volume ratio has been studied. D is determined by the laser flash method for a temperature of 50 °C. Measurements were carried out in duplicate for each sample, so the values shown in Figure 9 are the average of the two measurements.

A thermal diffusivity of $0.146 \text{ mm}^2.\text{s}^{-1}$ is obtained for PEKK alone. This value is in agreement with the literature on polymers^{24,30,31}: thermal diffusivity, at ambient temperature, is between 0.15 and $0.2 \text{ mm}^2.\text{s}^{-1}$ with a value of $0.2 \text{ mm}^2.\text{s}^{-1}$ for PEEK.²¹ Introduction of carbon into the PEKK matrix led to an increase in thermal diffusivity. The diffusivity does not follow a linear variation: this complex behavior will be described later by analog model. The PEKK/GC composite (45 vol % of carbon) reaches a value of $0.626 \text{ mm}^2.\text{s}^{-1}$.

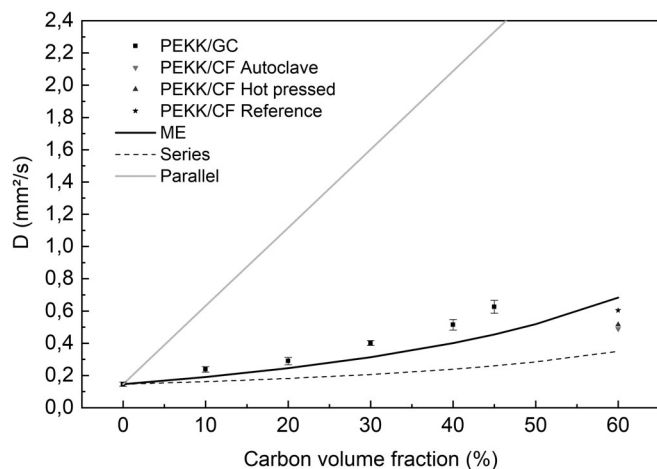


Figure 10. Thermal diffusivity D as a function of the carbon volume content. The gray and black continuous lines correspond to the parallel and Maxwell-Eucken models respectively; the dashed line corresponds to the series model.

The increase in the thermal diffusivity by the addition of GC is rather weak considering the thermal diffusivity of a compacted powder of GC, which is reported in the literature²² between 4 and $10 \text{ mm}^2.\text{s}^{-1}$. Several PEKK/CF samples (40 vol % of PEKK) were studied by the laser flash method at 50 °C. The diffusivity results for these samples are reported in Table III.

For the composite “PEKK/CF reference,” a value of $0.603 \text{ mm}^2.\text{s}^{-1}$ is measured. This value is considered as the optimum diffusivity value obtainable with this type of PEKK composite. Measurements were also made on a PEKK/CF composite sample consolidated in autoclave. The samples produced by laser deposit have a thermal diffusivity lower than the reference composite, which implies a better consolidation of the reference composite. Thermal diffusivity, in the same way that the thermal conductivity, increases with the consolidation level. A diffusivity of $0.495 \text{ mm}^2.\text{s}^{-1}$ is obtained for the consolidated autoclave composite and a value of $0.603 \text{ mm}^2.\text{s}^{-1}$ is obtained for the reference composite. This implies that the internal connectivity of the material plays a major role in the speed of phonon diffusion.

Isothermal Analog Model. Analog models used for thermal conductivity were adapted to thermal diffusivity by keeping the volume percentage of the two constituents (ν_1 and ν_2) and replacing the thermal conductivity by the diffusivity (D_1 and D_2). The values D_2 and ν_2 being associated with the most thermally conductive constituent; here, the carbon (GC or CF). For all three models the value of D_1 is $0.146 \text{ mm}^2.\text{s}^{-1}$ (polymer value) and the value of D_2 is $6 \text{ mm}^2.\text{s}^{-1}$. The different analog models, as well as the experimental thermal diffusivity points of the PEKK/GC and PEKK/CF composites, are shown in Figure 10.

The parallel model is well above our experimental points, as for thermal conductivity, the measurement is not in the longitudinal direction of oriented carbon layers. The series model is below the experimental points corresponding to PEKK/GC composites. The diffusivity values of PEKKCF hot pressed composites are close to the series model, which is consistent with transversal measurement of successive layers of PEKK and continuous carbon fibers. The

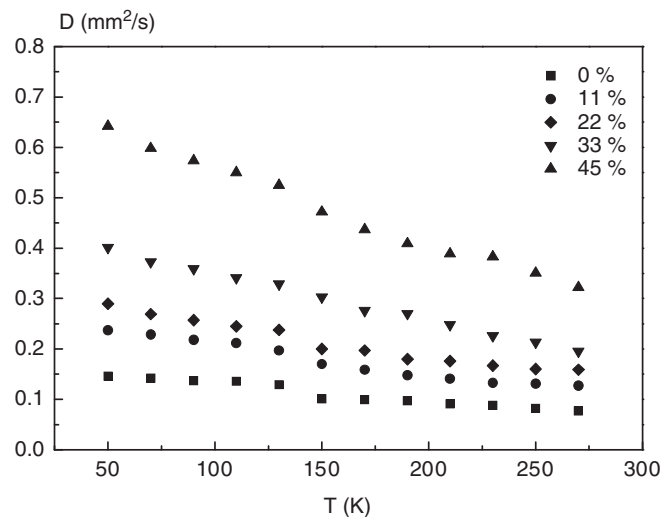


Figure 11. Thermal diffusivity D of PEKK/GC composites as a function of temperature.

Table IV. Analytical Parameters Describing the Thermal Diffusivity D Behavior as a Function of Temperature

$D = a.T + b$	$a (\times 10^{-4})$	b
PEKK	-3.44	0.165
PEKK/11% GC	-5.59	0.265
PEKK/22% GC	-6.25	0.311
PEKK/33% GC	-9.28	0.443
PEKK / 45% GC	-14.5	0.702

laser-deposited composite shows a behavior close to the serial model, with the autoclaved PEKK/CF sample showing a thermal diffusivity of $0.495 \text{ mm}^2 \cdot \text{s}^{-1}$ and the hot-pressed PEKK/CF sample showing a thermal diffusivity of $0.517 \text{ mm}^2 \cdot \text{s}^{-1}$. The higher thermal diffusivity for the reference composite with fiber, $\lambda_{\text{Ref}} = 0.603 \text{ mm}^2 \cdot \text{s}^{-1}$, corresponds to a behavior closer to the Maxwell–Eucken model. This behavior is explained by a better consolidation and also by a better distribution of the matrix between the fibers which implies an homogeneous dispersion of disk (corresponding to carbon fiber seen in 2D). The case of spherical particle dispersion in a matrix can explain the proximity with the Maxwell–Eucken model. In the case of composites produced by laser deposit, the lower thermal diffusivity is explained by a poor distribution of the matrix in the fibers, which would give rise to differentiated layers of fiber and polymer (as in the case of the series model). The experimental points of the PEKK/GC are well described by the Maxwell–Eucken model which confirms that the dispersion of the particles within the PEKK matrix is good.

Evolution with Temperature

Filler Content Effect. The effect of carbon particles on the PEKK thermal diffusivity was studied on the PEKK/GC composites as a function of temperature. The measurements were performed on composites loaded between 0 vol % and 45 vol % of carbon, for temperatures between 50 and 270 °C. Measurements were carried out in duplicate and the values reported in Figures 11 are the average of these two sets of data.

Thermal diffusivity slowly decreases with temperature for all samples. A quasi-linear decrease in thermal diffusivity with temperature has already been observed for PEEK/carbon particle composites.^{17,21} The increase in temperature induces a greater thermal agitation which causes a greater number of collisions between phonons. The concomitant decrease of the average free path results in a decrease of D. The slope increases gradually with the volume fraction of carbon used; to study this evolution an affine relationship was used. Analytical parameters describing the behavior of thermal diffusivity are reported in Table IV.

An increase in the absolute value of the slope is observed when increasing the amount of glassy carbon in the composite, which implies a stronger decrease of D with T. The increase in the amount of particles causes an increase in the number of interfaces which limits the average free path of the phonons: a faster decrease in the thermal diffusivity is thus easily explained.

Thermomechanical History Effect. The thermal diffusivity of consolidated PEKK/CF consolidated in autoclave and reference PEKK/CF composite were studied versus the temperature for three samples. Figure 12 shows the averages obtained for three samples.

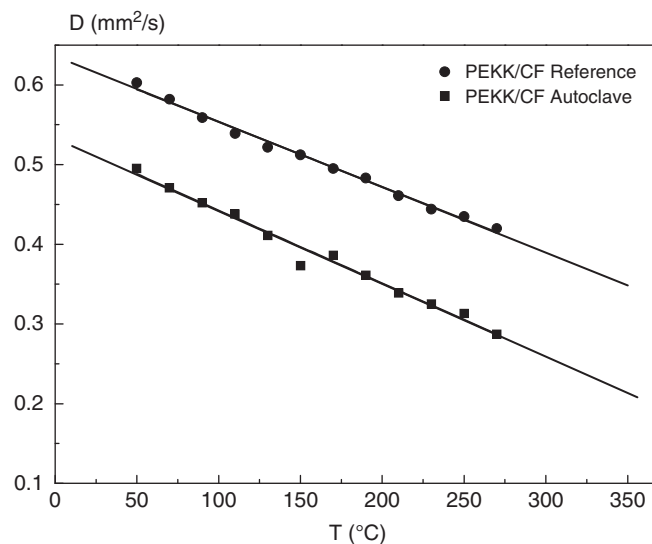


Figure 12. Thermal diffusivity D of PEKK/CF composites as a function of temperature.

The diffusivity values obtained for PEKK/CF (between 0.5 and $0.6 \text{ mm}^2 \text{ s}^{-1}$ at 50 °C) are very close to those reported for epoxy/continuous CF composites ($0.45\text{--}0.55 \text{ mm}^2 \text{ s}^{-1}$ at 50 °C).^{34–36} It is also interesting to note that the diffusivity values for PEKK/CF are slightly lower than the values obtained with PEEK/short-carbon fiber composites ($0.7\text{--}1 \text{ mm}^2 \text{ s}^{-1}$ at 50 °C).²¹ This difference has been attributed to the random orientation of the short fibers. As for spherical carbon particles, a monotonic decrease is observed on PEKK/CF composites in the temperature range studied. The experimental points of PEKK/CF composite consolidated in autoclave and the reference PEKK/CF are described by an affine equation with a slope of -9.15×10^{-4} and -8.15×10^{-4} , respectively.

Thermal diffusivity values, as well as the slope values, obtained for the PEKK/CF composites are lower than those obtained for the highest loading PEKK/GC composites. The lower diffusivity values are related to the transverse configuration of the fibers compared to measurement orientation. As for the slope values, they could be related to the interfacial resistances less important with the fibers than for the spherical particles.

CONCLUSION

In this study, the physical parameters associated with heat transfer have been studied for PEKK, PEKK/GC, and PEKK/CF composites. In PEKK/GC composites, thermal conductivity and diffusivity show an increase with the addition of carbon fillers. For low carbon ratio, the Maxwell–Eucken model indicates from experimental data that particles are well dispersed. For higher carbon ratio, experimental data are no more consistent with the Maxwell–Eucken model. This discrepancy might be explained by contacts between carbon particles, which are not taken into account by the model. The effect of porosity on conductivity and thermal diffusivity is strongly marked on PEKK/CF composites. The decrease in porosity causes an increase in thermal parameters: this evolution is due to an increase in the internal connectivity of the composite. The increase in λ and D implies other parameters than porosity. The

reference PEKK/CF composite approaches the theoretical model of Maxwell–Eucken, which implies in a 2D transverse section, a homogeneous dispersion of disks in PEKK. Accordingly, it is important to emphasize that the thermal conductivity and diffusivity are dependent on the dispersion of fibers in PEKK/CF composites.

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